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(54) **Gasoline additive concentrate**

(57) The present invention is a gasoline additive concentrate which remains liquid at low temperatures of

about 0°F which contains a fatty acid, ester or mixtures thereof in combination with an alcohol, an amine or a mixture thereof.

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Description

The present invention relates to a gasoline additive concentrate containing solubilizers to maintain the concentrate in the liquid state at low temperatures.

U.S. Patent 4,617,026 is directed to a method for reducing the fuel consumption in an automotive internal combustion engine by employing a gasoline fuel containing an effective fuel consumption reducing amount of an additive which is a hydroxyl-containing ester of a monocarboxylic acid and a glycol or trihydric alcohol, said ester additive having at least one free hydroxyl group.

U.S. Patent 5,279,626 is directed to a fuel additive concentrate having an enhanced shelf life, the concentrate comprising a major amount of detergent/dispersant, a minor amount of demulsifier and an amount of solvent stabilizer sufficient to enhance the shelf life of the fuel additive package. The solvent stabilizer is formed from at least one aromatic hydrocarbon solvent and at least one alkyl or cycle alkyl alcohol wherein the solvent stabilizer composition contains more than 50 wt% aromatic hydrocarbon solvent and 10 to less than 50 wt% alcohol. The demulsifiers include organic sulfonates, polyoxyalkylene glycols, oxyalkylated phenolic resins and the like. Other components can be present in the concentrate including anti-oxidants, corrosion inhibitors, emission control additives, lubricity additives, antifoamants, biocides, dyes, octane or cetane improvers and the like. Corrosion inhibitors include dimers and trimer acids such as those produced from tall oil fatty acids, oleic acid, linoleic acid, and the like.

Most gasolines are additized by injecting a homogeneous, low viscosity and liquid additive concentrate into the gasoline while it is being loaded into trucks at the terminal rack. Commonly such additives are diluted in an aromatic solvent (e.g., xylene, aromatic 100, heavy aromatic naphtha) to produce a homogeneous, low viscosity fluid which is suitable for rack injection.

Obviously, the additive solution must be fluid, homogenous and low viscosity under all atmospheric conditions encountered at such outdoor truck loading facilities. Unfortunately, additives such as Tolad 9103 (a mixture of polymerized fatty acids, non-polymerized fatty acids and heavy aromatic naphtha, commercially available from Petrolite Corp.) is not suitable for additization under low temperature. It turns solid by 0°F within one day.

It has been discovered that fatty acids, oligomers of such acids and the esters of such acids, useful as anti friction and wear reducing additives in gasoline and diesel fuels are formulated into an additive concentrate which remains liquid at low temperatures of about 0°F and lower by the additional presence in the concentrate of an alcohol, an amine or a mixture of alcohol and amine. The fatty acids and their esters are typically derived from naturally occurring fats and oils and includes those known as tall oil acids and their esters.

The concentrate comprises fatty acids, oligomers of fatty acids, their esters and mixtures thereof in an aromatic solvent diluent and further a C₂ to C₁₀ alcohol, preferably a C₂ to C₈ alcohol, most preferably ethanol, which remains liquid at temperatures of at least as low as 0°C (32°F), a C₁₂ to C₇₅ amine having at least one nitrogen, preferably a C₁₂ to C₁₈ amine and which has a glass transition temperature or is liquid at temperatures of at least as low as 0°C (32°F), and mixtures of such alcohols and amines.

The concentrate comprises a lubricity additive selected from the group consisting of saturated or unsaturated fatty acids, oligomerized saturated or unsaturated fatty acids, primarily dimerized and trimerized acids, their esters and mixtures thereof, preferably the acid(s), in an aromatic solvent, preferably an aromatic solvent of 8 to 14 carbons, the acid(s), ester(s) or mixture thereof being present in the solvent in an amount of about 85 wt% or less, preferably about 50 wt% or less, more preferably 30 wt% or less, and a compatibilizer selected from the group consisting of an alcohol, an amine or a mixture thereof wherein, the alcohol or amine, preferably alcohol, used individually is present in an amount of at least about 30 wt% preferably about 35 wt%, more preferably about 40 wt% most preferably about 50 wt% based on the acid(s), ester(s) or mixture thereof, preferably when the lubricity additive component concentration in the diluent is about 50 wt% or less, preferably about 30 wt% or less, most preferably about 30 wt%, and the combination alcohol plus amine is used in an amount of about 10 wt%, preferably about 10 to 50 wt%, more preferably about 10 to 20 wt% based on the acid(s), ester(s) or mixture thereof, preferably when the lubricity additive component concentration in the solvent is about 30 wt% and higher, preferably about 50 wt% and higher. The weight ratio of alcohol to amine in the mixture is preferably about 2:10 to 10:1, more preferably 3:10 to 10:5 most preferably 1:1.

The invention is further understood with reference to the following examples.

EXAMPLE 1

The data tabulated below (Table 1) (blends 17 and 18) demonstrate that additional aromatic solvent (i.e., Aromatic 100 an aromatic solvent with an average carbon number between 9 and 11) does not effectively keep Tolad 9103 lubricity additive in the fluid state. There may be some very high level of aromatic solvent which may be sufficient to keep Tolad 9103 fluid at low temperatures. However, in practice it is desirable to keep the total amount of injected material at a minimum. This reduces transportation cost of the total package. Typical injection systems also have a maximum injection volume capacity. Large amounts of volatile aromatic solvents are also undesirable from an envi-

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ronmental viewpoint. They increase air discharge of volatile organic compounds.

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TABLE 1ALL COMPATIBILITY TESTS DONE AT 0°F

Blend No.	Aromatic 100 gms	T9103 gms	Alcohol Type	Alcohol gms	Amine type	Amine gms	Status after 3 days	Status after 7 days	Status after 13 days
17	10	3	none		none		ppt	ppt	ppt
18	10	5	none		none		ppt	ppt	ppt

EXAMPLE 2

The following blends (Table 2) contain 10 grams of Aromatic 100 solvent and 3 grams of Tolad 9103 in addition to various compatibilizing agents. Data below demonstrate that alcohol is an effective compatibilizer of Tolad 9103. Exxal 8 (iso-octanol) and ethanol are both effective. In addition, BASF Pluradyne FD-100 (poly isobutenyl monoamine having approximately 70 carbons) is also very effective. Hitec4956, a mannich base polyamine fuel detergent sold by Ethyl, is partially effective. Armeen HT-97 an amine which is not liquid at room temperature, did not function as a compatibilizer. Ethomeen C/12 is an ethoxylated cocoa alkylamine purchased from Akzo Chemical Co.

TABLE 2

Blend No.	Aromatic 100 gms	T9103 gms	Alcohol Type	Alcohol gms	Amine Type	Amine gms	Status after 3 days	Status after 7 days	Status after 13 days
1	10	3	none		FD100	1	no ppt	no ppt	no ppt
2	10	3	none		Ethomeen C/12	1	film	ppt	ppt
3	10	3	none		Hitec	1	no ppt	no ppt	ppt
4	10	3	Exxal 8	1	none		no ppt	no ppt	no ppt
5	10	3	none		S600 N *	1	ppt	ppt	ppt
7	10	3	none		Armeen HT-97	1	ppt	ppt	ppt
8	10	3	EtOH	1	none		no ppt	no ppt	no ppt
17	10	3	none		none		ppt	ppt	ppt

* S600 N is not an amine. It is a lubricating oil base stock.

TABLE 2 (continued)

Blend No.	Aromatic 100 gms	T9103 gms	Alcohol Type	Alcohol gms	Amine Type	Amine gms	Status after 3 days	Status after 7 days	Status after 13 days
22	10	3	Exxal 8	0.5	Armeen HT-97	0.5	no ppt	ppt	ppt
23	10	3	Exxal 8	0.5	FD100	0.5	no ppt	no ppt	no ppt
24	10	3	Exxal 8	0.5	Ethomeen C/12	0.5	ppt	ppt	ppt
25	10	3	Exxal 8	0.5	Hitec	0.5	no ppt	ppt	ppt
29	10	3	EtOH	0.5	Armeen HT-97	0.5	ppt	ppt	ppt
30	10	3	EtOH	0.5	FD100	0.5	no ppt	no ppt	no ppt
31	10	3	EtOH	0.5	Ethomeen C/12	0.5	film	ppt	ppt
32	10	3	EtOH	0.5	Hitec	0.5	no ppt	no ppt	no ppt

EXAMPLE 3

5 The following blends (Table 3) contain 10 grams of Aromatic 100 and 5 grams of Tolad 9103. The higher concentration of Tolad 9103 necessitates more compatibilizing agent. Only one compatibilizer was most effective. This was a 50/50 mixture of Ethanol and Ethomeen C/12. Note that this 50/50 mixture was less effective in the table above, when only 3 grams of Tolad 9103 was used. A repeat of this experiment confirmed that the combination of ethanol and Ethomeen C/12 is most effective with the higher dosage of Tolad.

10 Another compatibilizer which is partially effective in the table below is a mixture of Exxal 8 (iso-octanol) and Ethomeen C/12.

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TABLE 3

Blend No.	Aromatic 100 gms	T9103 gms	Alcohol Type	Alcohol gms	Amine Type	Amine gms	Status after 3 days	Status after 7 days	Status after 13 days
9	10	5	none		FD100	1	ppt	ppt	ppt
10	10	5	none		Ethomeen C/12	1	ppt	ppt	ppt
11	10	5	none		Hitec	1	ppt	ppt	ppt
12	10	5	Exxal 8	1	none		ppt	ppt	ppt
13	10	5	none		S600 N *	1	ppt	ppt	ppt
15	10	5	none		Armeen HT-97	1	ppt	ppt	ppt
16	10	5	EtOH	1	none		ppt	ppt	ppt
18	10	5	none		none		ppt	ppt	ppt
19	10	5	Exxal 8	0.5	FD100	0.5	ppt	ppt	ppt
20	10	5	Exxal 8	0.5	Ethomeen C/12	0.5	no ppt	ppt	ppt

* S600 N is not an amine. It is a lubricating oil base stock.

TABLE 3 (continued)

Blend No.	Aromatic 100 gms	T9103 gms	Alcohol Type	Alcohol gms	Amine Type	Amine gms	Status after 3 days	Status after 7 days	Status after 13 days
21	10	5	Exxal 8	0.5	Hitec	0.5	ppt	ppt	ppt
26	10	5	EtOH	0.5	FD 100	0.5	ppt	ppt	ppt
27	10	5	EtOH	0.5	Ethomeen C/12	0.5	no ppt	no ppt	no ppt
28	10	5	EtOH	0.5	Hitec	0.5	ppt	ppt	ppt
42	10	5	--	--	FD100	1.7	thick	--	--
43	10	5	--	--	Ethomeen C/12	1.7	ppt	--	--
44	10	5	--	--	Hitec	1.7	ppt	--	--
45	10	5	Exxal 8	1.7	--	--	no ppt	--	--
47	10	5	--	--	Armeen H-97	1.7	ppt	--	--
48	10	5	EtOH	1.7	--	--	no ppt	--	--

EXAMPLE 4

The data tabulated below (Table 4) demonstrate that the compatibilizer is best if it contains more than 1 part alcohol to 9 parts amine.

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TABLE 4

Blend No.	Aromatic 100 gms	T9103 gms	Alcohol Type	Alcohol gms	Amine type	Amine gms	Status after 3 days	Status after 7 days
33	10	5	EtOH	.1	Ethomeen C/12	.9	ppt	ppt
34	10	5	EtOH	.3	Ethomeen C/12	.7	no ppt	no ppt
35	10	5	EtOH	.7	Ethomeen C/12	.3	no ppt	no ppt
36	10	5	EtOH	.9	Ethomeen C/12	.1	no ppt	no ppt

EXAMPLE 5

The data tabulated below (Table 5) demonstrate that the most preferred compatibilizer is effective at low concentrations. The concentration of amine plus alcohol compatibilizer should be about 3 parts or more compatibilizer to 25 parts lubricity additive.

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TABLE 5

Blend No.	Aromatic 100 gms	T9103 gms	Alcohol Type	Alcohol gms	Amine type	Amine gms	Status after 3 days	Status after 7 days
37	10	5	EtOH	.4	Ethomeen C/12	.4	no ppt	no ppt
38	10	5	EtOH	.3	Ethomeen C/12	.3	no ppt	no ppt

The additive concentrate may, of course, contain other typical components such as detergents, carrier fluids, octane

boosters, antioxidants, metal corrosion inhibitor (especially copper corrosion inhibitors), and the like.

Claims

1. A gasoline lubricity additive concentrate comprising a lubricity additive selected from saturated and unsaturated fatty acids, oligomerized saturated and unsaturated fatty acids, esters of such fatty acids and of oligomerized fatty acids and mixtures thereof in an aromatic solvent, said lubricity additive being present in the solvent in an amount of about 85 wt% or less, and containing a compatibilizer which remains liquid to a temperature of at least about 0°C (32°F) selected from alcohol, amine and mixtures thereof wherein the alcohol or amine when used individually is present in an amount of at least about 30 wt% based on the weight of lubricity additive and wherein when the alcohol and amine are mixed, the combination of alcohol and amine is used in an amount of about 10 to 50 wt% based on the weight of lubricity additive.
2. The concentrate of claim 1 wherein the alcohol is a C₂ to C₁₀ alcohol.
3. The concentrate of claim 1 or claim 2 wherein the amine is a C₁₂ to C₇₅ amine having at least one nitrogen atom.
4. The concentrate of any preceding claim wherein the amine or alcohol, when used individually, is present in an amount of at least about 35 wt% based on lubricity additive.
5. The concentrate of any preceding claim wherein the compatibilizer is amine present in an amount of at least about 30 wt% based on lubricity additive when the lubricity additive concentration in the aromatic solvent is about 30 wt% or less.
6. The concentrate of any of claims 1, 2 or 3 wherein the compatibilizer is a combination of alcohol and amine, the weight ratio of alcohol to amine being from about 2:10 to 10:1.
7. The concentrate of any of claims 1, 2, 3 or 6 wherein the compatibilizer is a combination of alcohol and amine used at a concentration of at least about 10 wt% based on lubricity additive when the lubricating additive concentration in the aromatic solvent is about 30 wt% or higher.
8. The concentrate of any preceding claim wherein the lubricity additive is selected from saturated and unsaturated fatty acids, oligomerized saturated and unsaturated fatty acids and mixtures thereof.
9. The concentrate of any of claims 1 to 7 wherein the lubricity additive is selected from the esters of saturated and unsaturated fatty acids, esters of oligomerized saturated and unsaturated fatty acids and mixtures thereof.



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EUROPEAN SEARCH REPORT

Application Number
EP 96 30 9357

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	DE 42 25 951 A (LEUNA-WERKE) * claims 1-7 *	1-3,5-8	C10L1/14
X	EP 0 482 253 A (ETHYL) * page 10, line 1 - line 20 *	1,2,4,8	
X	US 4 565 547 A (TAKADA) * the whole document *	1-9	
A	FR 1 399 466 A (ESSO) * page 5, column 2 *	1,3-5,9	
A	US 4 797 134 A (VATARU) * the whole document *	1,3-5,8	
A	WO 95 02654 A (VICTORIAN CHEMICAL INT. PTY) * the whole document *	1,2,4,8,9	
A	US 4 451 265 A (SCHWAB) * the whole document *	1-9	
A	WO 95 03377 A (EXXON) * the whole document *	1-9	
D,A	US 5 279 626 A (CUNNINGHAM ET AL.) * column 2, line 39 - line 62 * * column 6, line 1 - line 10 *	1-9	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
The present search report has been drawn up for all claims			C10L
Place of search THE HAGUE		Date of completion of the search 19 March 1997	Examiner De La Morinerie, B
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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